BIODEGRADABLE ORIENTED AROMATIC POLYESTER FILM AND METHOD OF MANUFACTURE

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Inventor: KAKU MUREO (JP); MIZUTANI AKIKO (JP); MOTOMATSU MAKOTO (JP)
Applicant: DU PONT (US)
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The present invention relates to an oriented aromatic polyester film and a method of manufacture thereo The film is biodegradable, transparent and heat-sealable, and has excellent mechanical properties. The film comprises an acid component that is about 50 to 90 mol % terephthalic acid, about 0.2 to 6 mol % sulfonic acid metal salt, and about 4 to 49.8 mol % aliphatic dicarboxylic acid; and a glycol component that is about 50 to 99.9 mol % ethylene glycol and about 0.1 to 50 mol % diethylene glycol. The film has an impulse seal strength and a high-frequency seal strength of at least 3 N/15 mm. In addition, the film also has low moisture vapor transmission, oxygen transmission and carbon dioxide transmission, and ha ultrasonic sealability.

BIODEGRADABLE ORIENTED AROMATIC POLYESTER FILM AND METHOD OF MANUFACTURE

Description of correspondent: **WO0110928**

TITLE OF INVENTION
BIODEGRADABLE ORIENTED AROMATIC POLYESTER FILM
ANDMETHOD OF MANUFACTURE
CROSSREFERENCED TO RELATED APPLICATIONS
This application claims priority benefit from Japanese patent application No. 11 (99)-225660, filed August 9,1999.

BACKGROUND OF THE INVENTION
FIELD OF THE INVENTION
The present invention relates to a biodegradable oriented aromatic polyester film and a method for manufacturing the film. The invention relates more particularly to an oriented aromatic polyester film and its manufacture, which film is biodegradable, transparent and heat-sealable by conventional sealing techniques such as impulse sealing, high-frequency sealing and ultrasonic sealing. The film has selectively low moisture vapor transmission, low oxygen or carbon dioxide transmission to meet the requirements of a gas barrier necessary for packaging materials, and is endowed with excellent mechanical strength, making it highly suitable for use in such applications as packaging materials.

DESCRIPTION OF RELATED ART
Prompted by societal concerns and demands concerning the disposal of plastic products such as plastic films, research is being done on biodegradable resin compositions. Active efforts are underway to develop biodegradable aromatic polyester resin compositions which are degradable under the high-humidity, hightemperature conditions associated with waste composting processes. Various uses are being proposed for such compositions. For example, the published Japanese translations of PC patent applications (designated hereinafter by the Japanese term 'Tokuhyo') 5-507109,6-505513 and 6-505040 describe polyesters prepared by polymerizing a glycol component made of ethylene glycol and diethylene glycol with two acid components; namely, an alkali metal or alkaline earth metal salt of a sulfonic acid, and terephthalic acid. These prior-art references also describe fibers, films, sheets and fiber nonwoven fabrics composed of such polyesters.

JP-A 6-23836 and JP-A 7-205278 describe biodegradable films and methods for their production, which films are biaxially oriented films produced by melt-extruding a biodegradable polylactic acid polymer as a film then orienting the extruded film. Such films have properties similar to those of films endowed with good strength and clarity, such as oriented polypropylene film, oriented polystyrene film and oriented polyethyleneterephthalate film.

Tokuhyo 5-508819 discloses a film of improved properties,including strength, stiffness and clarity, that is formed by extruding a polyhydroxy acid composition, then carrying out stretching treatment to give a biaxially oriented film.

Films made of ordinary resins such as polyolefin resins, polyamide resins, polyester resins and polyvinyl chloride resins are currently widely used today as packaging materials.

When films formed of degradable polymer are used as packaging materials and in related applications, the relevant properties (e. g., mechanical strength, clarity and gas barrier properties) of the films generally fall somewhat short of the properties of resins that have hitherto been used in packaging materials, such as polyolefm resins, polyamide resins, polyester resins and polyvinyl chloride resins.

As noted above, oriented films made of polylactic acid resins have improved strength and clarity. Yet, they continue to lack sufficient stiffness, impact resistance, heat-sealability and gas barrier properties for practical use.

Moreover, when a film is extruded using polylactic acid, and especially poly (L-lactic acid), the melting point is170 C. Because the temperature difference with the glass transition temperature (about60 C) and with the crystallization temperature (about110 C) is small, the allowable range of conditions for carrying out orientation is narrow. Hence, film composed of this type of resin is poorly suitable for orientation.

BRIEFSUMMARY OF THE INVENTION

It is therefore an object of the invention to provide an oriented aromatic polyester film which is biodegradable, transparent and heat-sealable, highfrequency sealable and ultrasonically sealable, and which has selectively low moisture vapor transmission, low oxygen or carbon dioxide transmission and also excellent orientation properties, film strength and gasbarrier properties. Such a film should further have excellent mechanical properties such as strength, stiffness and impact resistance, as exhibited by polyethylene terephthalate.

Another object of the invention is to provide a method for manufacturing oriented aromatic polyester films which has a broad range of suitable orientation conditions and presents no problem in production of the film.

Applicants have found that an oriented aromatic polyester film having excellent mechanical properties such as strength, stiffness and impact resistance can be obtained by forming a film from a polyester copolymer having repeating units composed of terephthalic acid, a sulfonic acid salt, an aliphatic dicarboxylic acid, ethylene glycol and diethylene glycol, then subjecting the formed film to orientation.

Accordingly, the invention provides an oriented aromatic polyester film comprising an aromatic polyester copolymer having repeating units comprising an acid component which is about 50 to 90 mol % terephthalic acid, about 0.2 to 6 mol % sulfonic acid metal salt and about 4 to 49.8 mol % aliphatic dicarboxylic acid, and a glycol component which is about 50 to 99.9 mol % ethylene glycol and about 0.1 to 50 mol % diethylene glycol. The film has at least one of an impulse seal strength and high-frequency seal strength of at least 3N/15 mm.

The invention also provide an oriented aromatic polyester film having moisture vapor transmission not greater than150g/m2*d, oxygen transmission not greater than300 cc/g m2*d-atm, carbon dioxide transmission not greater than 1000 cc/gm2-d-atm. Moreover, the film may be ultrasonically sealable.

The invention further provides a method for manufacturing an oriented aromatic polyester film having an impulse seal strength and a high-frequency seal strength of at least 3 N/15 mm. The method comprises the steps of preparing an aromatic polyester copolymer having repeating units comprising an acid component and a glycol component, wherein the acid component is about 50 to 90 mol % terephthalic acid, about 0.2 to 6 mol % sulfonic acid metal salt and about 4 to 49.8 mol % aliphatic dicarboxylic acid, and the glycol component is about 50 to 99.9 mol % ethylene glycol and about 0.1 to 50 mol % diethylene glycol; forming the aromatic polyester copolymer into an unstretched film; and orienting the unstretched film.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, there is provided an oriented aromatic polyester film comprising an aromatic polyester copolymer. The copolymer has repeating units comprising an acid component and a glycol component. The acid component is about 50 to 90 mol %, and preferably, about 52 to 83 mol %, terephthalic acid.

Further according to the present invention, the acid component is about 0.2 to 6 mol%, and preferably about 2 to 5 mol%, sulfonic acid metal salt. Illustrative examples of the sulfonic acid metal salt include metal salts of 5-sulfoisophthalic acid, metal salts of 4-sulfoisophthalic acid, and metal salts of 4-sulfophthalic acid. Of these, metal salts of 5-sulfoisophthalic acid are preferred. Preferred examples of the metal ions include ions of alkali metals such as sodium, potassium and lithium, or of alkaline earth metals such as magnesium. The most preferred sulfonic acid metal salt is the sodium salt of 5-sulfoisophthalic acid.

The sulfonic acid metal salt is not only relatively expensive, when used in excess it renders the polyester water-soluble and moreover affects physical characteristics such as film shrinkage. The sulfonic acid metal saltsignificantly contributes to the degradability of the resulting film even at a low content of 0.2 mol %.

Further according to the present invention, the acid component is about 4 to 49.8 mol %, and preferably about 10 to 45 mol %, aliphatic dicarboxylic acid. At less than 4 mol %, the glass transition temperature cannot be significantly lowered.

On the other hand, an aliphatic dicarboxylic acid level in excess of 49.8 mol % invites a decline in the glass transition temperature, causing a loss of suitable stiffness in the film.

The aliphatic dicarboxylic acid preferably has 2 to 18 carbons, and more preferably 2 to 10 carbons. Illustrative examples include azelaic acid, succinic acid, adipic acid, sebacic acid and glutaric acid. Of these, glutaric acid is preferred.

Composting that involves the degradation of plastic film is typically carried out under high-temperature, high-humidity conditions. Because this is generally done at a temperature of about70 C or less, the polyester should have a glass transition temperature (Tg) not higher than preferably about70 C, and especially about65 C. In the invention, an aliphatic dicarboxylic acid is used to set the glass transition temperature not higher than about70 C.

An ester-forming derivative of the dicarboxylic acid, such as the dimethyl ester, may be used in place of the dicarboxylic acid.

The glycol component is about 50 to 99.9 mol % ethylene glycol and about 0.1 to 50 mol % diethylene glycol, and preferably about 80 to 98 mol % ethylene glycol and about 2 to 20 mol % diethylene glycol. More than 50 mol % of diethylene glycol units adversely influences the mechanical properties of the film, such as the tensile strength, whereas less than 0.1 mol % results in poor degradability.

The glass transition temperature may be further lowered by substituting up to 20 mol % of the ethylene glycol with another glycol such as triethylene glycol.

A balanced range of properties, especially mechanical properties andbiodegradability, can be achieved by preparing the film of the present invention by choosing selected amounts of respective components within the above mol% ranges.

If it is desired to enhance the mechanical properties of the film, the amount of terephthalic acid is increased, and if it is desired to enhance biodegradability, the amount of aliphatic dicarboxylic acid is increased, resulting in a lower glass transition temperature(Tg).

The aromatic polyester polymer used to form the inventive film can generally be prepared by any well-known polymerization method. For example, a straight-chain polyester in which the monomer units are randomly distributed along the molecular chain can be prepared by charging a polymerizer with all of the above monomer constituents together with antimony or some other catalyst, and carrying out polycondensation under suitable polycondensation conditions. Another method that may be used involves initially reacting two or more of the monomer constituents to prepare a prepolymer, then adding the remaining monomer constituents andpolymerizing.

The aromatic polyester polymer used to form the film of the invention decomposes under the high-humidity, high-temperature conditions typical of composting. Most of the monomer and oligomer (i. e., terephthalic acid, glycol, and oligomers thereof) which forms as a result of such degradation is readily digested by microorganisms in the solid wastes or compost, ultimately becoming carbon dioxide and water.

Conventional additives such as plasticizers, lubricants, inorganic fillers, antioxidants and weathering stabilizers may be added to the foregoing aromatic polyester polymer for the purpose of adjusting the film formability or mechanical properties, provided the mechanical characteristics, degradability and other properties critical to the polyester are not altered thereby, and the resulting aromatic polyester composition subjected to film formation.

The polyester copolymer that forms the inventive film typically has an intrinsic viscosity within a range of 0.1 to 1.5, and preferably 0.3 to 1.2.

The oriented aromatic polyester film of the present invention has an impulse strength and a high-frequency seal strength of at least 3N/15 mm."Impulse seal strength,"as used herein, refers to the strength measured by the impulse seal method. According to this method, sealing is effected in a conventional manner by a conventional sealing apparatus. The sealing apparatus includes a nichrome wire having a 2 mm width. The sealing areas of separate sheets of films are overlapped and pressed with the nichrome wire while a pulsed current is passed through the wire to effect momentary heating and sealing of the film. The sealed film is then cut into 15 mm wide strips perpendicular to a seal bar, which is a part sealed in the films.

Using the test specimens thus prepared, the maximum strength of the sealing area is measured by means of a tensile test according to JIS K7127. This value is the impulse seal strength.

"High-frequency sealing"is a method for sealing in which the films subjected to sealing are heat-bonded by the heat generated inside the films when such films are placed in a high-frequency electric field. High-frequency sealing is measured by the same tensile test as described for impulse seal strength."Highfrequency seal strength refers"to the strength of the films prepared according to this

invention.

The film of the present invention has a moisture vapor transmission not greater than 150g/m2d, oxygen transmission not greater than 300 cc/gm2-datm, carbon dioxide transmission not greater than 1000 cc/gm2-d-atm. The film has an ultrasonic seal strength such that it is useful for use a packaging material.

The oriented aromatic polyester film of the invention is well-suited for use in a range of applications, including agricultural and horticultural supplies such as mulch film for farming and gardening use, seed tape, pesticide bags and composting waste bags; household supplies such as bags for kitchen scraps, water drainage bags, shopping bags, paper cups and paper dishes; business supplies such as coated paper for recycling paper products, printedlaminates, card covers, window envelopes, and cover film for printed paper; hygienic supplies such as paper diaper backing sheets, sanitary napkins, disposable gloves and laundry bags; and general packaging applications such as bottles, shrink films for various use, food packaging films and wrapping films.

Further in accordance with the present invention, there is provided a method for manufacturing an oriented aromatic polyester film. The method comprises the step of preparing an aromatic polyester copolymer having repeating units comprising an acid component which is about 50 to 90 mol % terephthalic acid, about 0.2 to 6 mol % sulfonic acid metal salt and about 4 to 49.8 mol % aliphatic dicarboxylic acid, and a glycol component which is about 50 to 99.9 mol % ethylene glycol and about 0.1 to 50 mol % diethylene glycol.

The method further comprises the step of forming an unstretched film using the above aromatic polyester polymer. The process of forming the unstretched film involves feeding aromatic polyesterpolymer-containing flakes to an extruder, melting the flakes, extruding the melt through a film die, then rapidly cooling the extruded material on a chill roll to form an unstretched film having a thickness within a range of about 5 to300 um. The film is then collected on a winding roll.

Next, the resulting unstretched film is oriented. The film is uniaxially oriented at a fixed width, consecutively biaxially oriented or simultaneously biaxially oriented within a temperature range defined by the glass transition temperature as the lower limit and the crystallization temperature as the upper limit, thereby giving an oriented aromatic polyester film having an impulse seal strength and high-frequency seal strength of at least 3N/15 mm.

The orientation step is carried out as follows. A set of nip rolls comprising a metal roll in association with a rubber roll, vacuum-type suction rolls, or both nip rolls and suction rolls are used as rotating rolls capable of providing the holding strength necessary to restrict the speed of film travel. The film that has been rapidly cooled after formation is passed through therotating rolls at a restricted speed to effect orientation in the machine direction (MD). The resulting MD-oriented film is introduced onto a tenter frame, both edges of the film in the transverse direction are engaged by tenter grippers, and the film is stretched in the transverse direction(TD) while traveling together with the tenter grippers. The film is then heat-treated at a temperature of 120 to160 C, giving a biaxially oriented polyester film. Orientation of the polyester film in the machine direction and the transverse direction may be carried out sequentially in this order or in the opposite order, or may be carried out simultaneously. Orientation in the machine direction followed by orientation in the transverse direction is generally preferred.

In thepractice of the invention, orienting the formed film serves to improve the inadequate film strength of the unstretched film, making it possible to achieve good film strength and clarity.

Orientation is carried out by suitable selection of the orientation conditions. The orientation temperature is set within a range of preferably 40 to100 C, and more preferably 60 to80 C. The stretch ratio is set within a range of preferably 1.5 to 6.0, and more preferably 2.5 to 6.0. Selecting a suitable stretch ratio is critical for increasing film strength, which is one of the objects of the invention. At a stretch ratio less than 1.5, the film strength is inadequate, whereas a stretch ratio greater than 6 results in a loss in film uniformity. Neither extreme is desirable.

After orientation, the film dimensions may be stabilized by administering heat treatment (heat setting). Carrying out heat treatment makes it possible to obtain an oriented film having good heat sealability.

EXAMPLES
Examples are given below by way of illustration, although the examples are not intended to limit the scope of the invention.

TESTMETHODS
The methods of measurement and evaluation used in the examples are described below.

Biaxial StretchFormabilitv:
When a biaxially oriented film was fabricated by carrying out biaxial stretch formation, longitudinal cracking (tearing) of the film during transverse orientation of the film on a tenter frame immediately after orientation in the machine direction was visually examined and rated according to the criteria indicated below.

Good: No film cracking (longitudinal tearing) was observed. Film remained stable at all times during transverse stretching.

Poor: Film cracking (longitudinal tearing) occurred. Film lacked stable transverse stretchability.

Modulus:
Measured in accordance with JIS K7127.

Stress at Break:
Measured in accordance with JIS K7127.

Elongation at Break:
Measured in accordance with JIS K7127.

Impact Strength :
This is a stabbing-type impact test for thin packaging materials which was carried out in accordance with the puncture test principles described in
JIS P8134. A spindle fitted with a hemispherical (1.0-inch diameter) tip was brought up from below against a horizontally stretched circular specimen having a fixed surface area. The force at which the specimen ruptured was read off with a maximum reading pointer.

Haze:
Measured in accordance with JIS K6714.

Trans.

Measured in accordance with JIS K6714.

Impulse Seal Strength :
Measured by the impulse seal method. In this method, the sealing areas of separate sheets of films are overlapped and pressed with the nichrome wire having a 2 mm width while a pulsed current is passed through the wire to effect momentary heating and sealing of the film. The sealed film is then cut into 15 mm wide strips perpendicular to a seal bar, which is a part sealed in the films. Using the test specimens thus prepared, the maximum strength of the sealing area is measured by means of a tensile test according to JIS K7127.

High-Frequencv Seal Strength :
Measured by the high-frequency sealing method. In this method, the films subjected to sealing are heat-bonded by the heat generated inside the films when such films are placed in a high-frequency electric field.High-frequency sealing is also measured by the tensile test according to JIS K7127.

Moisture vapor transmission
Measured in accordance with JIS K7129(40 C, 90% RH).

Gas transmission
Measured in accordance with JIS K7126(20 C, 60% RH).

SoilDesradability:
Test pieces of a given size were placed in soil for 5 months, following which the specimens were visually examine.

EXAMPLES
Example 1
Flakes (small particles) of an aromatic polyester copolymer (density,
1.35g/cm3; melting point,200 C; melt index at220 C under 2,160 g of loading, 25 g/10 min) having repeating units composed of an acid component that is about 50 to 90 mol % terephthalic acid, about 0.2 to 6 mol % sodium5-sulfoisophthalate and
about 4 to 49.8 mol % glutaric acid, and a glycol component that is about 50 to 99.9 mol % ethylene glycol and about 0.1 to 50 mol % diethylene glycol were predried in an oven, then melted in a 60 mm diameter

extruder at a cylinder temperature setting of 200 to220 C. The melt was extruded through a T-die and rapidly cooled (to30 C) on cast rolls to form a 200
Measured/evaluatedpropertyExample1Comp.Ex.1Comp.Ex.2
<tb> Biaxialstretchformabilitygoodpoorgood
<tb> Modulus(MPa;MD/TD) <SEP> 200 <SEP> 5,200/5,400
<tb> Stressatbreak(MPa;MD/TD)130/130 <SEP> 100/120 <SEP> 210/220
<tb> Elongationatbreak(%:MD/TD)180/170 <SEP> 110/90 <SEP> 120/120
<tb> Impactstrength(J)0. <SEP> 8 <SEP> 0. <SEP> 9 <SEP> 1. <SEP> 0
<tb> TearStrength(N;MD/TD)0. <SEP> 35/0. <SEP> 1 <SEP> 0.25/0.15 <SEP> 0. <SEP> 15/0.15
<tb> Haze(%)1. <SEP> 0 <SEP> 1. <SEP> 2 <SEP> 3. <SEP> 0
<tb> Trans(%)90 <SEP> 93 <SEP> 88
<tb> Heatsealstrength(N/15mm)8. <SEP> 0 <SEP> 2. <SEP> 1 <SEP> 0
<tb> High-frequencysealstrength <SEP> 5. <SEP> 9 <SEP> 1. <SEP> 3 <SEP> 0
<tb> (N/15mm)
<tb> Ultrasonicsealstrength <SEP> 0. <SEP> 5 <SEP> 0. <SEP> 2 <SEP> 0. <SEP> 4
<tb> (N/mm)
<tb> Moisturevaportransmission8025020
<tb> (g/'d)
<tb> Oxygentransmission8080060
<tb> (cc/gm2-d-atm)
<tb> CO'transmission <SEP> 400 <SEP> 2500 <SEP> 300
<tb> (cc/gm2datm)
<tb> ShapereadilybreaksShapereadilybreaksNochange
<tb> DegradabilityinSoildownunderoutsidedownunderoutside
<tb> forcesforces
<tb>

On comparing the results obtained in Example 1 using a film according to the invention with the results obtained in Comparative Example 1 using a polylactic acid film, it is apparent that, although both films are biodegradable and have excellent strength, the film in Example 1 has an improved heat sealability, (as measured by heat seal strength) high-frequency sealability (as measured by high frequency seal strength) and ultrasonic sealability (as measured by ultrasonic seal strength) and much improved moisture vapor transmission, oxygen transmission and carbon dioxide transmission. Moreover, the results show that Example 1 has good stretching properties, and thus can be fabricated under a wide range of stretching conditions.

Comparing the results from Example 1 with those from Comparative
Example 2, it is found that the film in Example 1 has mechanical properties, optical properties, moisture vapor transmission, oxygen transmission and carbon dioxide transmission which make it useful as a packaging material. In addition, the film has an improved soil degradability, and heat sealability and high-frequency sealability.

Avantages of the Invention
The oriented aromatic polyester films of the invention are biodegradable, transparent, heat-sealable, high-frequency sealable, and ultrasonically sealable. In addition, the films also have low moisture vapor transmission, low oxygen transmission and low carbon dioxide transmission necessary for use as a packaging material. In addition, they have excellent mechanical properties such as strength, stiffness and impact resistance. These films thus lend themselves particular well to use as packaging materials. The method for manufacturing films of the invention involves the orientation of polyester film having excellent stretchability, and is therefore capable of manufacturing oriented aromatic polyester film under a broader range of orientation conditions than possible with prior-art biodegradable film.

BIODEGRADABLE ORIENTED AROMATIC POLYESTER FILM AND METHOD OF MANUFACTURE

Claims of correspondent: **WO0110928**

CLAIM (S)
What Is Claimed Is:
1. An oriented aromatic polyester film comprising an aromatic polyester copolymer having repeating units comprising an acid component and a glycol component, wherein the acid component is about 50 to 90 mol% terephthalic acid, about 0.2 to about 6 mol% sulfonic acid metal salt, and about 4 to 49.8 mol% aliphatic dicarboxylic acid; the glycol component is about 50 to 99.9 mol % ethylene glycol and about 0.1 to 50 mol% diethylene glycol; and the film has at least one of an impulse seal strength and a high-frequency seal strength of at least 3N/15 mm.

2. The film of claim 1, wherein the film has at least one of the following properties: moisture vapor transmission not greater than150g/m2-d, oxygen transmission not greater than 300cc/g m2d-atm and carbon dioxide transmission not greater than 1000cc/g m2-datm.

3. The film of claim 1, wherein the film has an ultrasonic seal strength of 0.5 N/mm.

4. The film of claim 1, wherein the film is biodegradable.

5. A method for manufacturing an oriented aromatic polyester film having at least one of an impulse seal strength and a high-frequency seal strength of at least 3N/15 mm, the method comprising the steps of :
(a) preparing an aromatic polyester copolymer having repeating units composed of an acid component and a glycol component, wherein the acid component is about 50 to 90 mol % terephthalic acid, about 0.2 to 6 mol % sulfonic acid metal salt and about 4 to 49.8 mol % aliphatic dicarboxylic acid, and the glycol component is about 50 to 99.9 mol % ethylene glycol and about 0.1 to 50 mol % diethylene glycol;
(b) forming the aromatic polyester copolymer into an unstretched film; and
(c) orienting the unstretched film.